

PATENT SPECIFICATION

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(54) PROCESS FOR THE PREPARATION OF A BINDER FOR USE IN PRINTING INK

(71) We, AKZO N.V., a Company organised and existing under the laws of the Kingdom of the Netherlands, of IJssellaan 82, Arnhem, the Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The present invention relates to a process for the preparation of a printing ink binder based on a cyclopentadiene resin modified with carboxylic acid and subsequently esterified. British Patent Specification No. 1,379,037 describes a binder obtained by reacting a cyclopentadiene resin with an unsaturated mono- or dicarboxylic acid, and esterifying the reaction product with a monovalent alcohol. This specification also mentions that esterification with a polyvalent alcohol is undesirable since the resulting solution is too viscous for use in a printing ink. A disadvantage of this known process is that modifying the cyclopentadiene resin with starting materials having a functionality not higher than 2 results in resins being obtained which hardly, if at all, cross-link and display an insufficiently rapid emission of solvent after application.

30 The binders of the present invention can be used successfully to prepare printing inks, more particularly rapid-drying rotogravure inks and offset inks. When used in rotogravure inks, the binders therefor must be very soluble in organic solvents such as toluene and/or petrol. When used in offset inks, the binders must be sufficiently soluble in high-boiling hydrocarbons having a low aromatics content and mixable with oxidatively drying components, such as linseed oil and air-drying alkyd resins. Both types of resulting printing inks must have a suitable application viscosity having regard to the desired binder concentration. Furthermore, the binder must possess a good pigment-wetting capacity and a high-softening point, for example, above 130°C. Finally, the printing ink film must be rub-proof and be of uniform and high quality.

The binder of the invention, or a printing ink prepared therefrom, satisfies the above-mentioned requirements. The binders of the invention, or a printing ink prepared therefrom, generally also have the properties of a rapid emission of solvent or solvent mixture, a short drying time, a high gloss and a brilliant colour.

Accordingly, the present invention provides a process for the preparation of a printing ink binder which comprises reacting a cyclopentadiene resin (as hereinafter defined) at a temperature in the range of from 120°C to 300°C with an ethylenically unsaturated dicarboxylic acid or an anhydride thereof, and with a monocarboxylic acid free of aliphatic unsaturation, having from 3 to 9 carbon atoms, and at least partly esterifying the acidic reaction mixture at a temperature in the range of from 140° to 300°C with one or more hydroxy and/or epoxy compounds having an average OH functionality in the range of 2.1 to 12.

By the term "cyclopentadiene resin" as used herein is meant a hydrocarbon-soluble resin obtained by polymerising a mixture containing at least 50% by weight of cyclopentadiene, dicyclopentadiene and/or an alkyl derivative thereof at a temperature in the range of 200° to 350°C, in the presence or not of an inert hydrocarbon as solvent. The monomer mixture to be polymerised may also contain compounds such as styrene, alkyl derivatives of styrene, indene or other compounds liberated in the cracking of petroleum fractions. Preferably, the resin should contain at least 70% by weight of cyclopentadiene, dicyclopentadiene and/or an alkyl derivative thereof, the alkyl group containing 1 to 4 carbon atoms. The softening point of the resin is generally in the range of from 50° to 210°C, and preferably in the range of from 70° to 140°C. The molecular weight of the resin is generally between 200 and 2000, and preferably between 300 and 1000.

The cyclopentadiene resin is generally reacted with a specific saturated monocarboxylic acid in an amount of from 0.01 to 1 mole, and preferably from 0.02 to 0.8 moles, per 100 grams of resin. The reaction is carried

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out at a temperature in the range of 120° to 300°C, and preferably 200° to 260°C. The reaction pressure is not critical; the reaction is usually carried out at atmospheric or elevated pressure. The reaction may be accelerated by using acidic catalysts, for example sulphuric acid, phosphoric acid, perchloric acid, boron trifluoride or complex compounds thereof; the use of a catalyst, however, is not absolutely necessary. It is believed that the addition of the saturated monocarboxylic acid (represented as RCOOH) to the cyclopentadiene resin takes place with formation of an ester group by coupling an RCOO group and an H atom respectively to 2 carbon atoms of the resin which are linked by a double bond.

By the introduction of ester groups which are directly attached to the cyclopentadiene resin the properties of the binder are surprisingly very much improved. Accordingly, improved properties such as a higher pigment wetting capacity, an improved solubility of the binder in an organic solvent and a better heat stability, so that the resin will discolor less upon heating, may be obtained.

Examples of suitable monocarboxylic acids are aromatic carboxylic acids, for example, benzoic acid; aliphatic carboxylic acids, for example, propionic acid, 2-methyl propionic acid, butyric acid, 3-methyl butyric acid, valeric acid, trimethyl propionic acid, caprylic acid, 2-ethyl caproic acid and trimethyl caproic acid; and cycloaliphatic monocarboxylic acids, for example, hexahydrobenzoic acid and naphthenic acid. Mixtures of monocarboxylic acids free of aliphatic unsaturation may also be used, if desired. Preferably, aliphatic monocarboxylic acids having from 6 to 9 carbon atoms are used, and in particular those having a branched carbon chain.

In the process of the present invention the cyclopentadiene resin is reacted in known manner with an ethylenically unsaturated dicarboxylic acid, or an anhydride thereof. In general, the reaction is carried out at temperatures in the range of 120° to 300°C, using 0.01 to 0.6 moles, preferably 0.02 to 0.4 moles, of the dicarboxylic acid or anhydride per 100 grams of the unmodified cyclopentadiene resin.

Examples of suitable ethylenically unsaturated dicarboxylic acids are maleic acid, methyl maleic acid, fumaric acid, itaconic acid, mesaconic acid, citraconic acid, tetrahydrophthalic acid and methyl tetrahydrophthalic acid or, if desired, the anhydrides of these acids. Mixtures of ethylenically unsaturated dicarboxylic acids and/or anhydrides thereof may also be used. Maleic anhydride is preferably used.

The reaction pressure is not critical; the reaction is generally carried out at atmospheric or elevated pressure. The reaction between the resin and the dicarboxylic acid, or anhydride thereof, may take place before, during or after the reaction of the resin with

the monocarboxylic acid free of aliphatic unsaturation. Alternatively, the dicarboxylic acid may be present during the preparation of the cyclopentadiene resin.

The cyclopentadiene may first be reacted with at least a portion of the monocarboxylic acid free of aliphatic unsaturation, particularly when the acid is used in a relatively large amount, and subsequently with the ethylenically unsaturated dicarboxylic acid, or anhydride thereof, and with the remaining portion, if any, of the monocarboxylic acid.

After reaction of the cyclopentadiene resin with carboxylic acid, the acidic reaction mixture is at least partly esterified with one or more hydroxy and/or epoxy compounds whose average OH functionality is in the range of from 2.1 to 12, and preferably in the range of from 2.2 to 4.5 (hereinafter referred to as polyol compound).

The amount of polyol compound employed is dependent on the mean carboxyl functionality and on the total number of carboxyl groups of the acidic reaction mixture and is generally between 0.02 and 1.8 moles per 100 grams of non-modified cyclopentadiene resin.

Examples of suitable hydroxy and/or epoxy compounds, provided that the mixture of these compounds has a mean OH functionality of 2.1 to 12, are monovalent alcohols such as propanol, isopropanol, butanol, nonanol, cyclohexanol, benzyl alcohol; divalent alcohols such as ethylene glycol, propylene glycol, 2,2-dimethyl - 1,3 - propane diol, 2 - methyl - 2-phenyl - 1,3 - propane diol, diethylene glycol, cyclohexane diol, 1,2 - bis - hydroxymethyl - cyclohexane, 1,4 - bis - hydroxymethyl - cyclohexane, 2,2 - bis - (4 - hydroxycyclohexyl) - propane, 1,1 - isopropylidenebis(paraphenylene - oxy)di - ethanol, 1,1 - isopropylidene - bis(paraphenylene - oxy)di - 2-propanol; polyvalent alcohols containing three or more hydroxyl groups per molecule such as glycerol, trimethylol propane, trimethylol ethane, 1,2,6 - hexane triol, pentaerythritol, di- and polypentaerythritol, sorbitol, inositol, epoxy compounds such as propylene oxide, glycidol, epoxy butane, epoxy alkyl esters of aliphatic, aromatic and cycloaliphatic monocarboxylic acids and compounds such as ethanol amine and triethanol amine.

The esterification reaction is carried out at temperatures in the range of from 140° to 300°C, and preferably in the range of from 160° to 280°C. The water formed in the esterification reaction may be removed in the known way, and is generally done by azeotropic distillation with the use of organic solvents such as toluene or xylene.

The modified cyclopentadiene resin may be even further modified by carrying out the esterification reaction in the presence of a phenol aldehyde resin. Preferably, a phenol formaldehyde resin of the resole type is used. The phenol resin is generally used in an

amount of from 1 to 60 parts by weight, and preferably in an amount of from 10 to 40 parts by weight per 100 parts by weight of modified cyclopentadiene resin. If desired, other compounds may be added to the reaction mixture during or after the reaction; for example: abietic acid, mineral oils, pigments, colourants, waxes, asphalt compounds, linseed oil, linseed stand oil and polymeric compounds, such as alkyd resins and chlorinated rubber.

The phenol resin may be prepared in a known manner from one or more phenols and one or more aldehydes in an alkaline medium at a temperature in the range of from 30° to 150°C. Example of suitable phenols are phenol, alkyl phenols, alkoxy phenols, alkaryl phenols, aralkyl phenols and bisphenols; the phenols generally have from 6 to 16 carbon atoms. Suitable aldehydes are, for example: formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde and isobutyraldehyde. The molar ratio of the phenol and the aldehyde is usually between 1:1 and 1:2.

The invention will be further described with reference to the following non-limitative Examples. In these Examples, the softening point was determined in accordance with the "ring and ball" method (ASTM method E 28-67), the colour was measured on a 50%-solution of the resin in toluene in accordance with ASTM method D 1544-68 (Gardner colour scale), and the viscosity was determined on a 50%-solution of the resin in toluene at 20°C.

EXAMPLE 1.

732 grams of a commercially available cyclopentadiene resin having a melting point of 85°C, and a colour 8 were melted in a flask and subsequently 356 grams (2.78 moles) of hexahydrobenzoic acid and 117.6 grams (1.2 moles) of maleic anhydride were mixed therewith. The mixture was then heated to 240°C and maintained at that temperature for 2 hours. Although no reaction water was formed at this stage, the acid number was found to have decreased. Subsequently, 207 grams (1.533 moles) of trimethylol propane were slowly added thereto, after which the mixture was allowed to react for 4 hours at 260°C. 1350 grams of clear resin were obtained having an acid number of 12.7, a viscosity of 280 cP, a softening point of 145°C and a colour 12. A rotogravure ink was prepared by mixing the pigment magenta with a toluene solution of the resulting resin and the mixture subsequently ground. At an application viscosity of 30 cP the weight ratio resin: toluene:magenta was 30:62.5:7.5. After printing on natural paper, the rotogravure ink showed a rapid solvent emission, a fast drying time, a high rub resistance and a good gloss.

EXAMPLE 2.

732 grams of a cyclopentadiene resin having

a melting point of 105°C and a colour 8 were melted in a flask and mixed with 76 grams (0.48 moles) of trimethyl caproic acid, 61.5 grams (0.48 moles) of hexahydrobenzoic acid and 58.8 grams (0.6 moles) of maleic anhydride. The resulting mixture was heated to 240°C in an inert gas atmosphere and at atmospheric pressure, at which temperature it was maintained for 2 hours. Subsequently, 64.8 grams (0.48 moles) of trimethylol propane and 12.5 grams (0.12 moles) of neopentyl glycol were added and the mixture heated to 260°C. After reaction for 4.5 hours at 260°C a clear, light-coloured resin was obtained, having an acid number of 13.5, a viscosity of 150 cP, a softening point of 152°C and a colour 10.

An offset-lithographic ink was prepared by mixing the pigment magenta with the above-described binder, an air-drying isophthalic alkyd resin with an oil length of 65 (available under the trade name Setalin V 428 and marketed by Kunstharsfabriek Synthese), and a mineral oil (marketed by Magic Bros under the trade name Magiesol 47) and the mixture subsequently ground. The weight ratio of binder:alkyd resin:mineral oil:pigment was 34:3.4:46:16.6 at an application viscosity of 250 P at 20°C. After printing on paper, the offset ink showed a good gloss, a brilliant colour, excellent rub resistance and a short drying time.

The binder prepared in this Example was processed in the manner described in Example 1 into a rotogravure ink which, after being printed on natural paper, had the same favourable properties as mentioned in Example 1.

EXAMPLE 3.

610 grams of a cyclopentadiene resin having a melting point of 85°C and a colour 7 were melted in a flask and subsequently mixed with 439 grams (3.6 moles) of benzoic acid and 98 grams (1.0 mole) of maleic acid. The resulting mixture was heated for 2 hours to 240°C under xylene reflux. Subsequently, 172.5 grams (1.25 moles) of pentaerythritol were added thereto. After 5 hours reaction at 260°C, the resin was kept under reduced pressure for 30 minutes to remove the remaining xylene. A clear, toluene-soluble resin having an acid number of 10, a viscosity of 260 cP, a softening point of 156°C and a colour 11 was obtained. A rotogravure ink made from this resin displayed excellent properties, especially with respect to its drying speed. For comparison purposes, this Example was repeated, except that an equimolar amount of stearic acid was used instead of benzoic acid. The resulting resin had an acid number of 11, a viscosity of 40 cP, a colour 14 and a very low softening point (40°C). Because of its low softening point, sticky surface and incomplete solubility in toluene, the resin was totally unsuitable for use as a binder for a rotogravure ink.

EXAMPLE 4.

610 grams of a cyclopentadiene resin having a melting point of 105°C and a colour 7 were melted in a flask and subsequently mixed with 240 grams (1.0 mole) of naphthenic acid and 98 grams (1 mole) of maleic anhydride. The mixture was heated for 2 hours at 240°C, after which 172.5 grams (1.25 moles) of pentaerythritol and 317 grams (2.6 moles) of benzoic acid were added thereto. The reaction mixture was maintained at 260°C for 5 hours, use being made of azeotropic distillation with the aid of xylene to accelerate the esterification reaction and to prevent sublimation of the starting materials. The resin mass was then kept under reduced pressure for another 30 minutes to remove the remaining xylene. A product was obtained which was soluble in aromatic solvents and had an acid number of 9, a viscosity of 350 cP, a softening point of 161°C and a colour 13. This resin also showed good properties for use in rotogravure inks.

EXAMPLE 5.

732 grams of a cyclopentadiene resin having a melting point of 82°C and a colour 8 were melted in a flask and subsequently mixed with 86.5 grams (0.6 moles) of 2-ethyl caproic acid and 73.2 grams (0.6 moles) of benzoic acid. The mixture was heated to 220°C for 2 hours under xylene reflux. Then, 127.6 grams (1.1 moles) of fumaric acid were added thereto and the mixture was heated to 240°C, at which temperature it was maintained for 2 hours. 151 grams (1.45 moles) of neopentyl glycol and 13.5 grams (0.1 mole) of trimethylol propane were then slowly added thereto. After 4 hours azeotropic distillation with xylene at 260°C, a resin was obtained having an acid number of 13, a viscosity of 180 cP, a softening point of 149°C and a colour 11.

EXAMPLE 6.

The procedure described in Example 5 was repeated. After the addition of the alcohols mentioned in this Example, however, 200 grams of an alkyl phenol resin condensate obtained by alkaline condensation of 1 mole of octyl phenol and 1.7 moles of formaldehyde were added over a period of 1 hour at a temperature of 180°C. The resulting product was a resin having an acid number of 10, a viscosity of 350 cP, a softening point of 165°C and a colour 12. The solubility of this product in aliphatic solvents was better than that of the product of Example 5 and, furthermore, the softening point and the viscosity were higher. Excellent results were obtained using an ink consisting of 29 grams of this resin, 61.5 grams of toluene and 7.5 grams of magenta, especially with regard to drying time, brilliance of colour and rub resistance.

EXAMPLE 7.

750 grams of a cyclopentadiene resin hav-

ing a melting point of 82°C and a colour 8 were melted in a flask and heated to 180°C. 48.8 grams (0.4 moles) of benzoic acid and 53 grams (0.55 moles) of maleic anhydride were added thereto with stirring. The contents of the flask were then heated to 240°C and maintained at this temperature for 1½ hours. Subsequently, 36 grams (0.27 moles) of trimethylol propane and 19 grams (0.137 moles) of pentaerythritol were slowly added thereto and the temperature dropped to 180°C. 90 grams of an alkyl phenol resin condensate as described in Example 6 were added over a period of 1 hour and at a temperature of 180°C, after which the reaction mixture was brought to a temperature of 260°C over a period of 2.5 hours. The reaction mixture was maintained at 260°C for 3 hours to give a resin having a softening point of 177°C, an acid number of 7.2, a viscosity of 230 cP and a colour 11. A printing ink based on this binder, toluene and magenta in a weight ratio of 31.5:61:7.5 showed good rotogravure ink properties.

WHAT WE CLAIM IS:—

1. A process for the preparation of a printing ink binder which comprises reacting a cyclopentadiene resin (as hereinbefore defined) at a temperature in the range of from 120°C to 300°C with an ethylenically unsaturated dicarboxylic acid or an anhydride thereof, and with a monocarboxylic acid free of aliphatic unsaturation, having from 3 to 9 carbon atoms, and at least partly esterifying the acidic reaction mixture at a temperature in the range of from 140°C to 300°C with one or more hydroxy and/or epoxy compounds having an average OH functionality in the range of 2.1 to 12.
2. A process as claimed in claim 1 wherein the monocarboxylic acid is used in an amount of from 0.01 to 1 mole per 100 grams of cyclopentadiene resin.
3. A process as claimed in claim 2 wherein the monocarboxylic acid is used in an amount of from 0.02 to 0.8 moles per 100 grams of cyclopentadiene resin.
4. A process as claimed in any one of claims 1 to 3 wherein the reaction with the monocarboxylic acid is carried out at a temperature in the range of from 200°C to 260°C.
5. A process as claimed in any one of the preceding claims wherein the monocarboxylic acid is an aliphatic monocarboxylic acid having from 6 to 9 carbon atoms.
6. A process as claimed in claim 5 wherein the aliphatic monocarboxylic acid has a branched carbon chain.
7. A process as claimed in any one of the preceding claims wherein the ethylenically unsaturated dicarboxylic acid, or anhydride thereof, is used in an amount of from 0.01 to 0.6 moles per 100 grams of cyclopentadiene resin.
8. A process as claimed in claim 7 wherein

the ethylenically unsaturated dicarboxylic acid, or anhydride thereof, is used in an amount of from 0.02 to 0.4 moles per 100 grams of cyclopentadiene resin.

- 5 9. A process as claimed in claim 7 or claim 8 wherein the ethylenically unsaturated dicarboxylic acid anhydride is maleic anhydride.

- 10 10. A process as claimed in any one of the preceding claims wherein the acidic reaction mixture is esterified with one or more hydroxy and/or epoxy compounds whose OH functionality is in the range of 2.2 to 4.5.

- 15 11. A process as claimed in any one of the preceding claims wherein the esterification reaction is carried out at a temperature in the range of from 160° to 280°C.

12. A process as claimed in any one of the preceding claims wherein the esterification reaction is carried out in the presence of a phenol aldehyde resin.

13. A process as claimed in claim 1 substantially as hereinbefore described with reference to any one of the Examples.

14. A binder when prepared by a process as claimed in any one of the preceding claims.

15. A printing ink which contains a binder as claimed in claim 14.

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